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DEVELOPMENT OF CHALCOPYRITE CRYSTALS FOR

NONLINEAR OPTICAL APPLICATIONS

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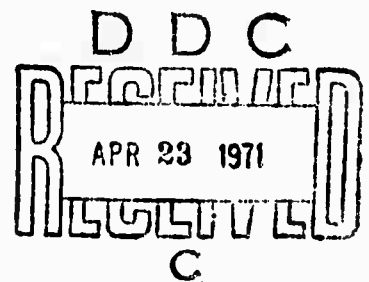M. L. Report No. 1933

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I. INTRODUCTION

During the past quarter considerable progress has been made in evaluating the optical constants of $CdGeAs_2$. The birefringence and dispersion have been measured allowing phasematching data to be calculated. The results show that $CdGeAs_2$ is phasematchable for SHG of the 10.6 μ CO_2 laser line. These results are discussed in Section III.

In addition to optical measurements, work has continued on the crystal growth problem. At the present time, a series of 30 samples are being prepared and evaluated to determine the equilibrium phase diagram for $CdGeAs_2$. The recent work in this effort is discussed in the next section.

In Section III we discuss the present experiment to measure by SHG the nonlinear coefficient of $CdGeAs_2$. We expect to have experimental results in the very near future.

From the progress during the past quarter we now know that $CdGeAs_2$ is phasematchable over its transparency range of 2.0 μ to 18 μ . In addition, from recent published data for $CdGeP_2$[1] we know that it also is phasematchable over most of its transparency region from .7 μ to beyond 10 μ . This suggests that $CdGeP_2$ may be very useful as an upconverter crystal. This potential use is discussed in Section V.

II. RECENT CRYSTAL GROWTH RESULTS

The research on $CdGeAs_2$ has centered on growth characterization and optical properties measurement. The growth techniques attempted have been satisfactory but considerable work remains to be done. At this time it appears that growth by the Bridgeman-Stockbarger technique gives the best results. We have obtained single crystals of sizes up to 4 mm^3. However, cracking and twinning does occur which hinders large sample growth. The present growth conditions which are near the optimum values are given in Table I. These conditions have yielded crystals that are relatively crack free and of high optical quality. However, the size of individual crystal regions is still small.

At the present time growth of large single crystals is prevented by the lack of growth characterization data. We do not know the $CdGeAs_2$ equilibirum phase diagram and therefore cannot correctly predict the proper constituent composition for growth. During the past six months we have investigated the (CdGe)-As plane of the ternary system. However, it appears that we must generalize and consider the complete ternary diagram. We therefore have started a growth and evaluation program aimed at determining the $Cd-Ge-As_2$ equilibrium phase diagram. This is necessary if growth progress is to be made for this crystal. In addition, it should provide a very good basis from which other chalco-pyrite crystals can be grown.

The crystal growth data is being evaluated by two techniques, Differential Thermal Analysis (DTA) and X-ray structure and micro-fluorescence analysis. These facilities are part of the central facilities

TABLE I

CdGeAs$_2$ GROWTH CONDITIONS

Synthesis	16 hr @ 740°
Treatment	Cd: etch 10% HNO$_3$
	Ge: polish HP-4
	As: none
Source	Cd, 6N; Ge, 7N; As, 6N
Weights	5.035 gr, Cd; 3.252 gr, Ge; 6.779 gr, As
Furnace	Bridgeman #2
Gradient	28°/cm
Crucible	Quartz 13 mm od, 4" long
Lower rate	0.12"/hour
ΔT/hr	8.5°/hour
Begin	4:00 pm 12/18/70
End	8:00 am 12/22/70

of the Center for Materials Research (CMR) at Stanford.

At present over thirty small samples have been grown over a range of compositions. These samples are analyzed for phase transitions, melting point, supercooling and crystal structure change. An example of a DTA run for $CdGeAs_2$ with 1% excess As is shown in Fig. 1. The top curve was taken during heating and shows a possible crystal structure change near $480^\circ C$, another at $624^\circ C$, and the melting point at $658^\circ C$. The $658^\circ C$ melting point compares well with the previously reported $665^\circ C$ melting point. Upon cooling, the crystal supercools considerably. The crystal structure change at the low temperature is also present.

At this time a number of DTA runs are be_ _g made to help establish the equilibrium phase diagram. With the assistance of the X-ray structure data and X-ray fluorescence analysis, the ternary phase diagram should be soluble.
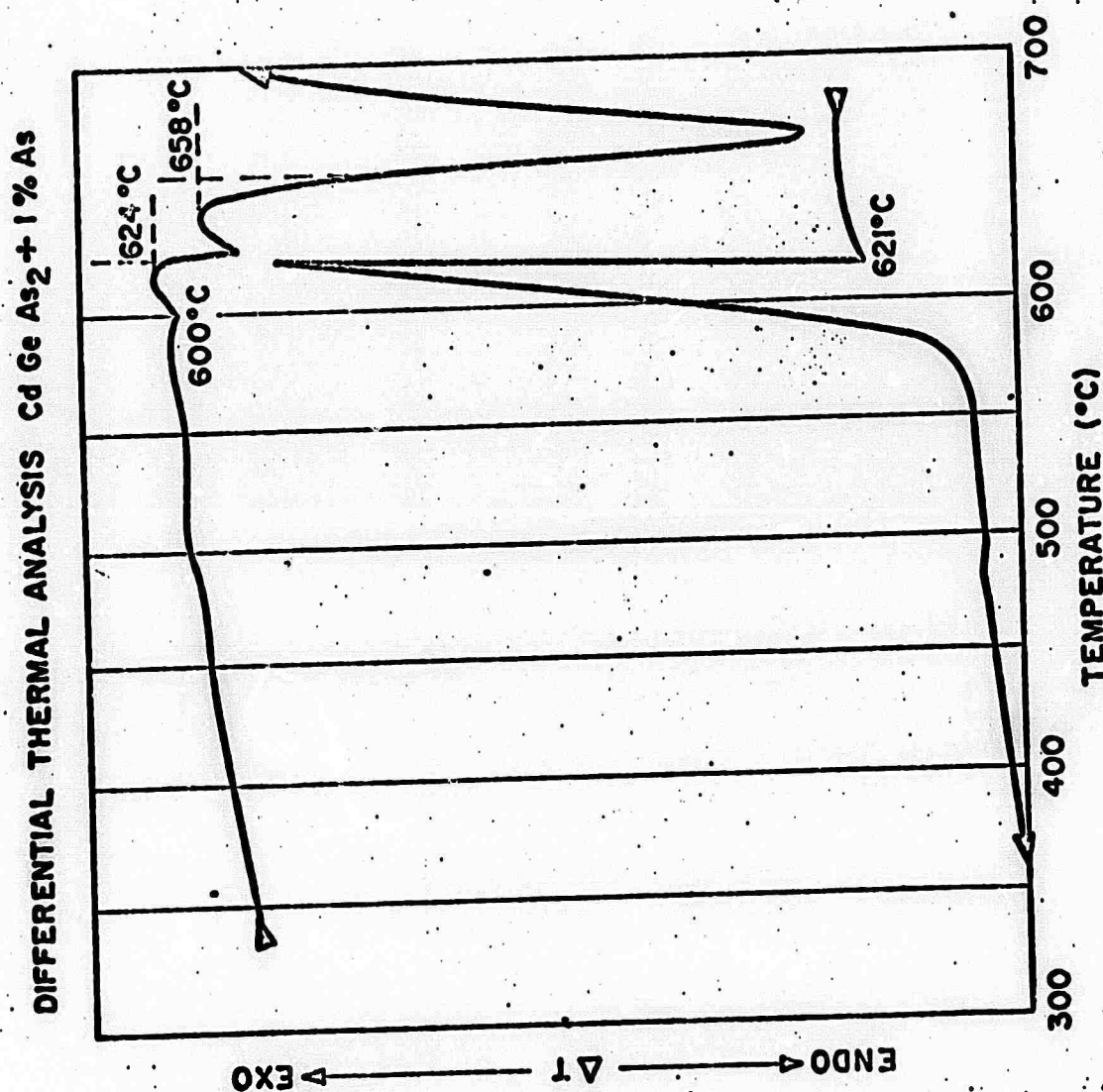
Fig. 1--Differential thermal analysis curve
for 1% excess As in CdGeAs₂ crystal.

III. OPTICAL PROPERTIES MEASUREMENT

We have been able to obtain optical data for $CdGeAs_2$ by using a single crystal prism. The sample was X-ray oriented and verified to be a single crystal. Using a plate of this material, a transmission measurement was made. Figure 2 shows the transparency range of a high quality sample of $CdGeAs_2$. The material is highly transparent out to 18 μ where two phonon absorption introduces appreciable absorption. Two phonon absorption also limits the long wavelength transmittance in GaAs and CdSe. Recent Russian work has also shown absorption due to two phonon interaction. From the transmittance data we expect that $CdGeAs_2$ will be a useful nonlinear crystal in the 2 μ to 18 μ region. It appears to be especially useful at 10.6 μ and for second harmonic generation (SHG) to 5.3 μ .

In estimating the usefulness of a nonlinear material for SHG or parametric processes in the optical or infrared region, it is necessary to know the nonlinear coefficient, transmission characteristics, and refractive index. Of these three properties, the refractive index must be known to the greatest accuracy since it is the birefringence and dispersion of a material that determines phasematching conditions and bandwidths for a nonlinear process. Also, since in most materials birefringence and dispersion are a function of temperature, pressure, and electric field, knowledge of these coefficients could be used to extend the phasematching region, provide a region of 90° phasematching, or tune a parametric process. Thus a method is needed to accurately determine refactive index as a function of various crystal parameters.
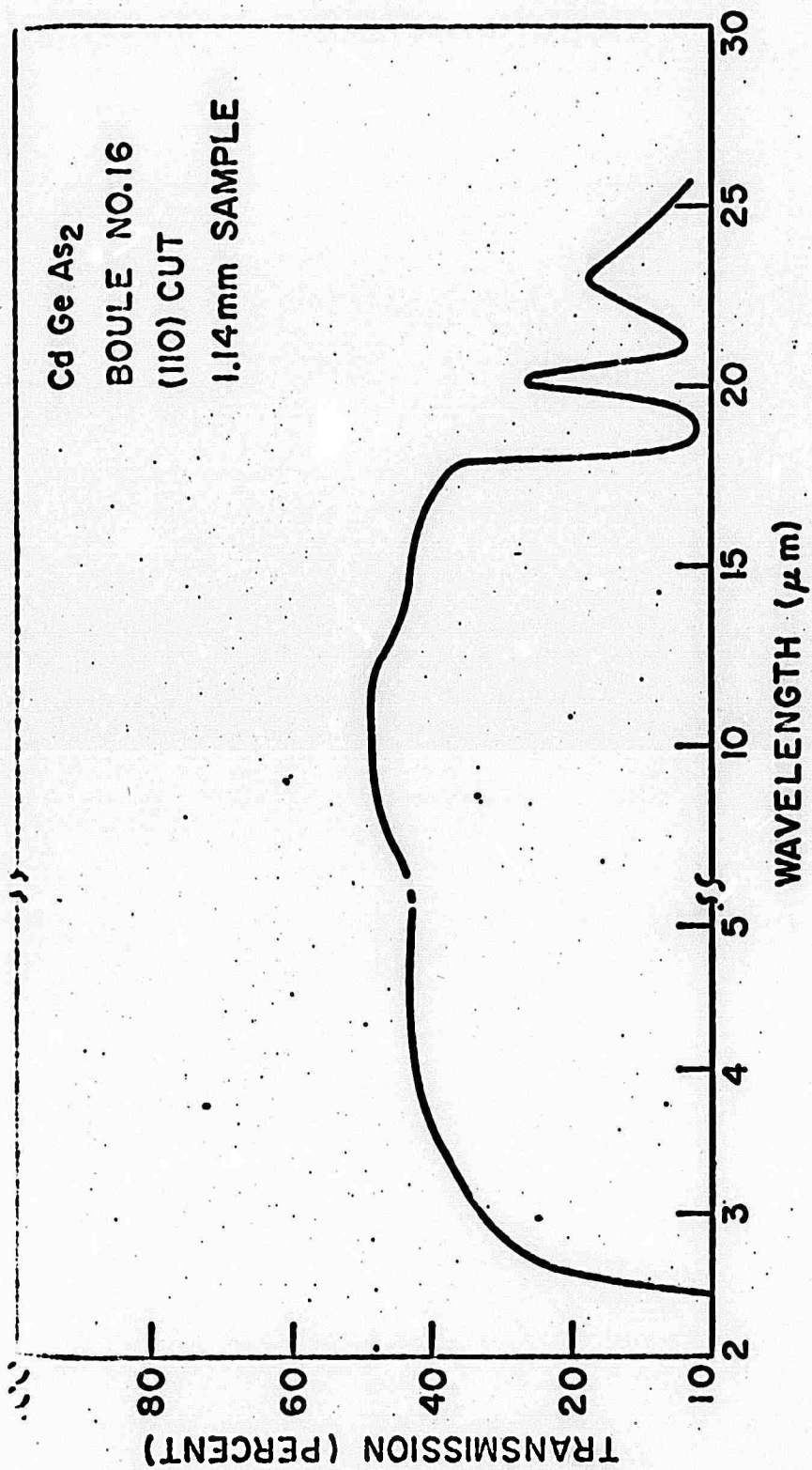
Fig. 2--Transmittance of a single crystal of CdGeAs$_2$. The two phonon absorption peaks are evident at 18 μ.

Figure 3 is a diagram of the apparatus we are constructing to accurately determine refractive index under various crystal conditions. The source can either be laser in the visible and infrared or a black body. The prism predisperser selects out a narrow band of wavelengths which then pass to the grating. By adjusting the slit width the band-pass of the grating can be set from .02 cm^{-1} to 2 cm^{-1}. The collimated output from the grating then passes through the crystal (in the shape of a prism) whose index is to be measured. The refracted beam from this crystal enters the collecting optics and is detected.

The crystal is mounted on a Gurley Unisec table from which angles can be measured directly to one second of arc. The apparatus is crystal size limited and for a crystal length (normal to the prism edge) of 1 cm the index can be measured to one part in the fourth decimal place in the near infrared region. The crystal mount is designed so that an electric field can be applied across the crystal or independently the crystal can be heated or cooled over a wide temperature range. Another mount is also available to measure the crystal's index as a function of pressure.

From these measurements very general Sellmeier equations can be derived which take into account variations of pressure, electric field, and temperature. Phasematching conditions can then be calculated accurately for SHG or parametric processes as a function of these variables.

With the prism properly cut and oriented, we have made the first high resolution measurements of optical index data for $CdGeAs_2$. We used a 3.39 μ HeNe laser and a 10.6 μ CO_2 laser as wavelength sources.

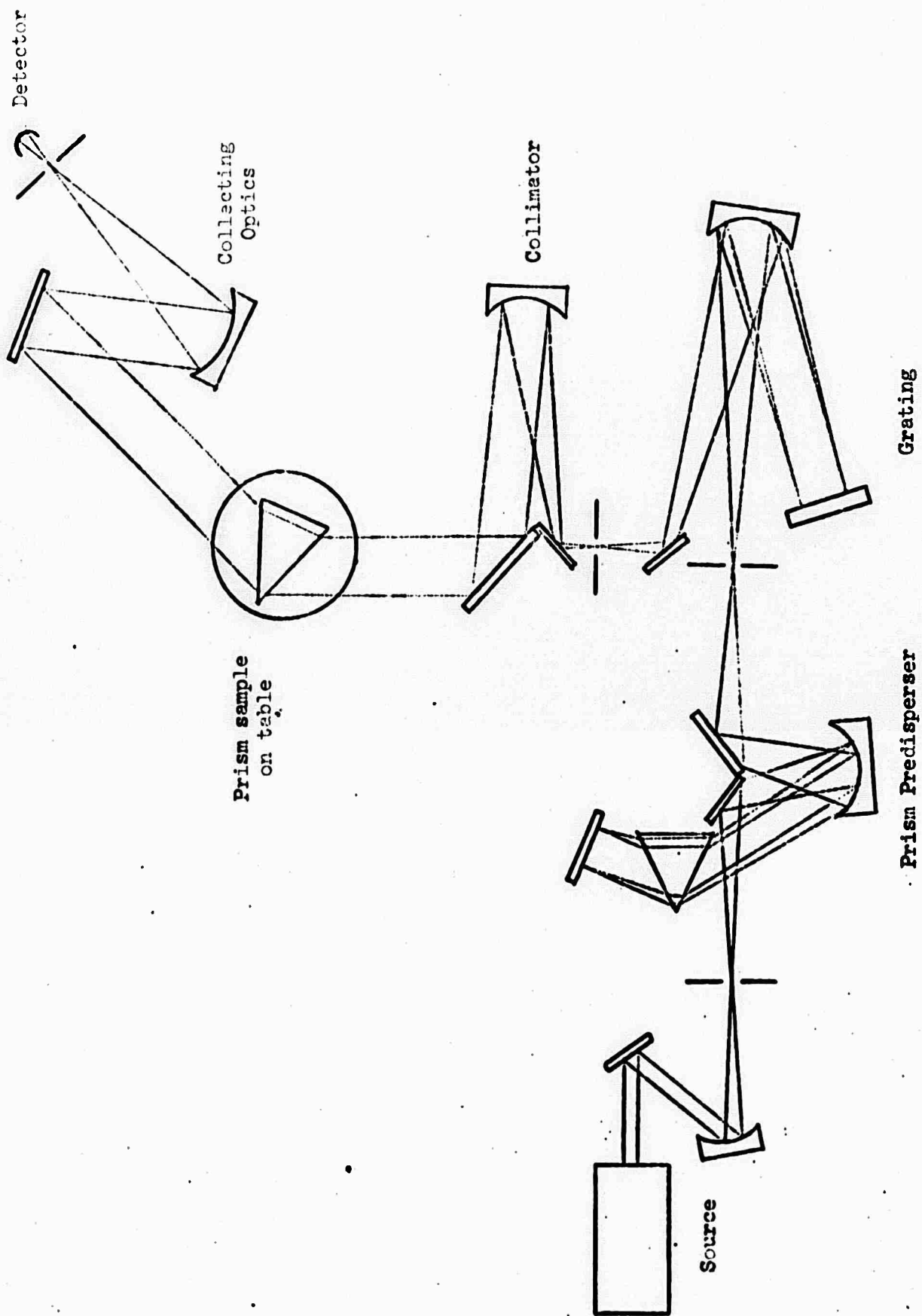The data obtained from these measurements is shown in Talbe II. This

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Fig. 3--Index of refraction measurement apparatus.

TABLE II

CdGeAs$_2$ INDEX OF REFRACTION

λ	n_o	n_e	Δn
3.39 μ	3.740	3.633	0.107
10.56 μ	3.568	3.474	0.094
5.3 μ (calculated)	3.658	3.565	0.093

data is very significant for a number of reasons. First, it shows that CdGeAs$_2$ is negative uniaxial $\left(n_o > n_e\right)$ which implies that Type I phasematching is possible. This allows the full use of the large 0.100 birefringence. Second, the birefringence is large and does allow phasematching. For SHG of 10.6 μ we require that $n_o(10.56\ \mu) > n_e(5.3\ \mu)$. From Table II we see that this condition is met.

Using the data in Table II we can fit the index of refraction data to a classical Sellmeier equation of the form

$$n^2 = 1 + \frac{\epsilon_{oo} - 1}{1 - (\lambda_{el}/\lambda)^2} + \frac{\epsilon_{DC} - \epsilon_{oo}}{1 - (\lambda_v/\lambda)^2}$$

where ϵ_{oo} and ϵ_{DC} are the relative dielectric constants at optical and dc frequencies and λ_{el} and λ_v are the wavelengths of the electronic and vibrational bands. From data available in the literature we know that $\epsilon_{DC} = 18.7$, $\lambda_{el} = 1\ \mu$, and $\lambda_v = 36\ \mu$. Using these results we can write a more generalized index equation

$$n^2 = A + \frac{B}{1 - (\lambda_{el}/\lambda)^2} + \frac{\epsilon_{DC} - A - B}{1 - (\lambda_v/\lambda)^2}$$

where $\epsilon_{DC} = A + B + C$ and $\epsilon_{oo} = A + B$. Finally, using the measured indices of refraction we find that

$$n_o^2 = 4.118 + \frac{9.056}{1 - (1/\lambda)^2} + \frac{5.526}{1 - (36/\lambda)^2}$$

and

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$$n_e^2 = 5.586 + \frac{7.000}{1 - (1/\lambda)^2} + \frac{6.114}{1 - (36/\lambda)^2}$$

for the ordinary and extraordinary indices of refraction.

This result now allows the calculation of phasematching angles and parametric oscillator tuning curves. Using the condition that

$$n_o(10.56 \ \mu) = n_e(\theta)$$

at 5.3 μ for SHG phasematching, we can calculate a phasematching angle θ . The result is

$$\theta = 79°24' .$$

We have oriented a plate of CdGeAs$_2$ and are attempting to verify this phasematching angle.

The usefulness of the chalcopyrite compounds for nonlinear optics is enhanced by their very large nonlinear coefficient. These coefficients have been previously measured by N. A. Goryunova et al.[1] in Russia by a reflection technique. The data shows that CdGeP$_2$ has $X_{NL} = 3.7 \ X_{NL}(GaAs)$ and that CdGeAs$_2$ has $X_{NL} = .50 \ X_{NL}(GaAs)$. This data is, however, not consistent with a figure of merit for a crystal based on Miller's nonlinear phenomenological rule that

$$\chi_{NL}^{(2\omega)} = \delta_{Miller}(\chi_L^\omega)^2(\chi_L^{2\omega})$$

where δ_{Miller} is a material constant and $\chi_L^{\omega} = (n^2(\omega) - 1)$ and $\chi_L^{2\omega} = (n^2(2\omega) - 1)$. If we assume that $\delta_{Miller}(CdGeAs_2) = \delta_{Miller}(CdGeP_2)$ and that this δ_{Miller} is also equal to that for GaAs, then we can write for the nonlinear susceptibility ratio that

$$\frac{\chi_{NL}^{2\omega}(CdGeP_2)}{\chi_{NL}^{2\omega}(GaAs)} = \frac{\left[(n^2(\omega) - 1)^2(n^2(2\omega) - 1)\right]_{CdGeP_2}}{\left[(n^2(\omega) - 1)^2(n^2(2\omega) - 1)\right]_{GaAs}}$$

and similarly for $CdGeAs_2$. Assuming that we are considering SHG of 10.6 μ to 5.3 μ , the ratio becomes

$$\frac{\chi_{NL}^{2\omega}(CdGeP_2)}{\chi_{NL}^{2\omega}(GaAs)} \approx 2.3$$

and

$$\frac{\chi_{NL}^{2\omega}(CdGeAs_2)}{\chi_{NL}^{2\omega}(GaAs)} \approx 2.0 \ .$$

This disagrees with the data presented in Ref. 1 for surface SHG using a Ruby laser. However, the experimental results are questionable due to the large absorption losses encountered. From the previous history of a very successful use of Miller's data to predict nonlinear coefficients, we expect that the above calculated nonlinear coefficient values are correct. Using these ratios and the recently measured absolute value for GaAs, we have the results shown in Table III.

Except for Te, which at the present time cannot be grown or obtained in high optical quality samples, the chalcopyrites have the largest available nonlinear coefficients for a phasematchable material. Since

TABLE III

NONLINEAR COEFFICIENTS

Material	Nonlinear coefficient (mks)	Relative to GaAs
KDP	5×10^{-24}	.0023
LiNbO$_3$	$.55 \times 10^{-22}$	.021
CdSe	1.44×10^{-22}	.125
HgS	$.44 \times 10^{-21}$	.38
Proustite	$.25 \times 10^{-21}$	.45
GaAs	1.14×10^{-21}	1.00
CdGeAs$_2$	2.28×10^{-21}	2.0
CdGeP$_2$	2.61×10^{-21}	2.3
Te	3.6×10^{-20}	31.5

the nonlinear interaction efficiency is proportional to the square of
the nonlinear coefficient, the chalcopyrite crystals appear to have
potentially 5 times more gain than GaAs. At this time parametric
processes in the infrared are limited by the lack of adequate gain. For
this reason these phasematchable chalcopyrite crystals assume a special
importance.

IV. SECOND HARMONIC GENERATION OF A 10.6 μ CO_2 LASER

Provided that good crystal quality can be obtained, $CdGeAs_2$ is potentially one of the best crystals available for SHG of 10.6 μ . The estimated nonlinear coefficient is twice GaAs and the phasematching angle is close to 90°. The corresponding walk-off angle is small. From Fig. 4 we have that the phasematching angle $\theta_m = 79^\circ 24'$. The walk-off angle ρ can be calculated from the expression

$$\tan \rho = \frac{n_o^2(\omega)}{2} \left[\frac{1}{n_e^2(2\omega)} - \frac{1}{n_o^2(2\omega)} \right] \sin 2\theta_m .$$

We obtain $\rho = 0.53^\circ$.

$CdGeAs_2$ has a $\bar{4}2m$ symmetry. This allows for type I phasematching. The components of the polarization along the principal axis are given by

$$P_x = 2 d_{14} E_y E_z$$

$$P_y = 2 d_{14} E_z E_x$$

$$P_z = 2 d_{36} E_x E_y$$

where according to the Kleinman symmetry condition $d_{14} = d_{36}$. The fundamental frequency is an ordinary wave polarized along the (110) axis and the second harmonic is an extraordinary wave. The phasematching angle can be determined by rotating the crystal around the polarization axis of the fundamental until maximum second harmonic output is obtained. We have cut two crystals both 1 mm thick with the c-axis oriented in the crystal plane for one and at 20° with respect to the
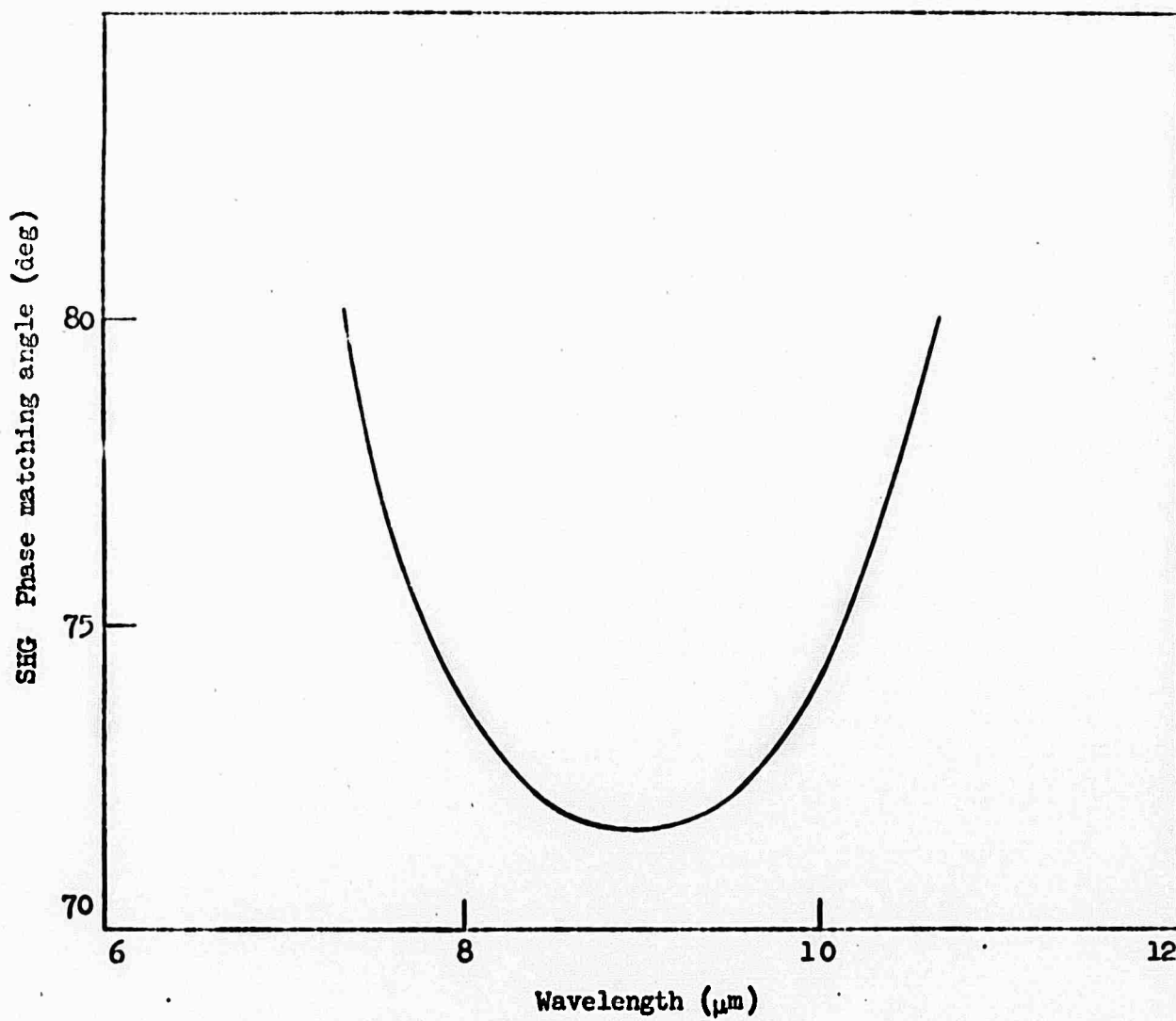
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Fig. 4 - Phasematching angle for SHG versus pump wavelength for CdGeAs$_2$.

crystal plane for the other. This allows us to search for a phasematching angle between 90° and approximately 55°. Rotating the crystal around the phasematching angle yields a sinc curve. The angular half-width can be estimated using the expression

$$\Delta\theta = \frac{\lambda}{2 l n_o(\omega)\rho}$$

which for a crystal length l equal to 1 mm yields

$$\Delta\theta \approx 10^{\circ} \quad .$$

The expression should, however, be used with some caution. It is only an approximation and for phasematching close to 90° higher order terms have to be included.

The CO_2 laser that we are using for the experiment yields up to 10 W of cw power in a Gaussian mode. The laser can also be Q-switched. For a high reflecting 10 m mirror, a cavity length of 133 cm, and a flat output mirror, the beam waist is

$$w_o = 3.38 \text{ mm} \quad .$$

Focussing with a Ge lens of a focal length $f = 3.93$ cm gives a beam waist inside the crystal of

$$w_1 \approx \frac{f\lambda}{\pi w_o} = 39.2 \ \mu \quad .$$

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This leads to a confocal parameter of

$$b = \frac{2\pi n_o(\omega) w_1^2}{\lambda} = 3.25 \text{ mm}$$

and an aperture length of

$$\ell_a = \frac{\sqrt{\pi}\, w_o}{\rho} = 7.8 \text{ mm} \quad .$$

Introducing the dimensionless parameters

$$\xi = \ell/b \quad \text{and} \quad B = \frac{\sqrt{\pi}}{2} \frac{\ell}{\ell_a} \xi^{-\frac{1}{2}}$$

in accordance with Ref. 2, we obtain for a crystal length of 1 mm

$$\xi = 0.31 \quad \text{and} \quad B = 0.206 \quad .$$

Since $B \ll 1$ the effect of double refraction is negligible. Since we also have $\xi \ll 1$, it follows that the SHG power is proportional to the crystal length squared and is given by the expression

$$P_2 = \frac{2 n_o^3 \omega_1^2 d_{36}^2 \sin^2\theta}{n_2 n_1^2} \frac{P_1^2}{\pi w_1^2} \ell^2 \quad .$$

Assuming 1 W of input power in the crystal and using the nonlinear coefficient in Table III, we obtain for the output power in the crystal

$$P_2 = 7.96 \times 10^{-5} \text{ W} \quad .$$

We are now setting up the experiment and plan to make the measurements within the next few days. The detector we presently are using is a liquid nitrogen cooled InSb detector with an active area of 0.5×0.5 mm^2. Due to this small area it is necessary to use a second lens to focus into the detector. Following the external SHG experiment we plan to try internal SHG of a Q-switched CO_2 laser. This should allow the construction of an efficient 5.3μ laser source which may then be useful as a pump for a $CdGeAs_2$ parametric oscillator.

The possibility of using $CdGeAs_2$ as an oscillator crystal has been investigated. We show in Fig. 5 the tuning curve and bandwidth for a 5.3μ pumped parametric oscillator. Tuning is accomplished by crystal rotation. Note that the curve covers the very important 8μ to 13μ atmospheric window.

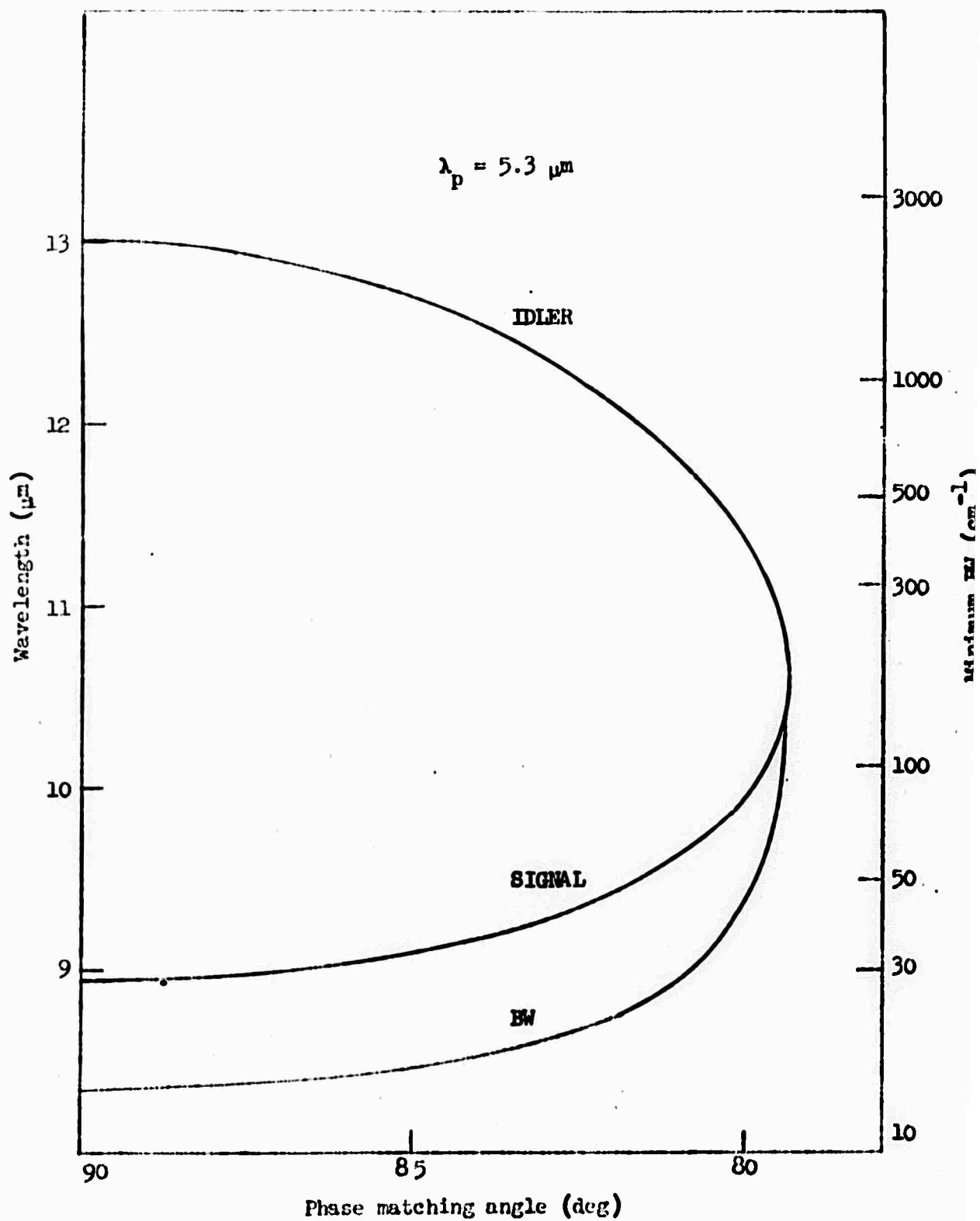Figure 6 shows additional tuning curves for other potential pump sources.

Fig. 5 - Bandwidth and tuning wave for 5.3 μ pumped CdGeAs$_2$ parametric oscillator.
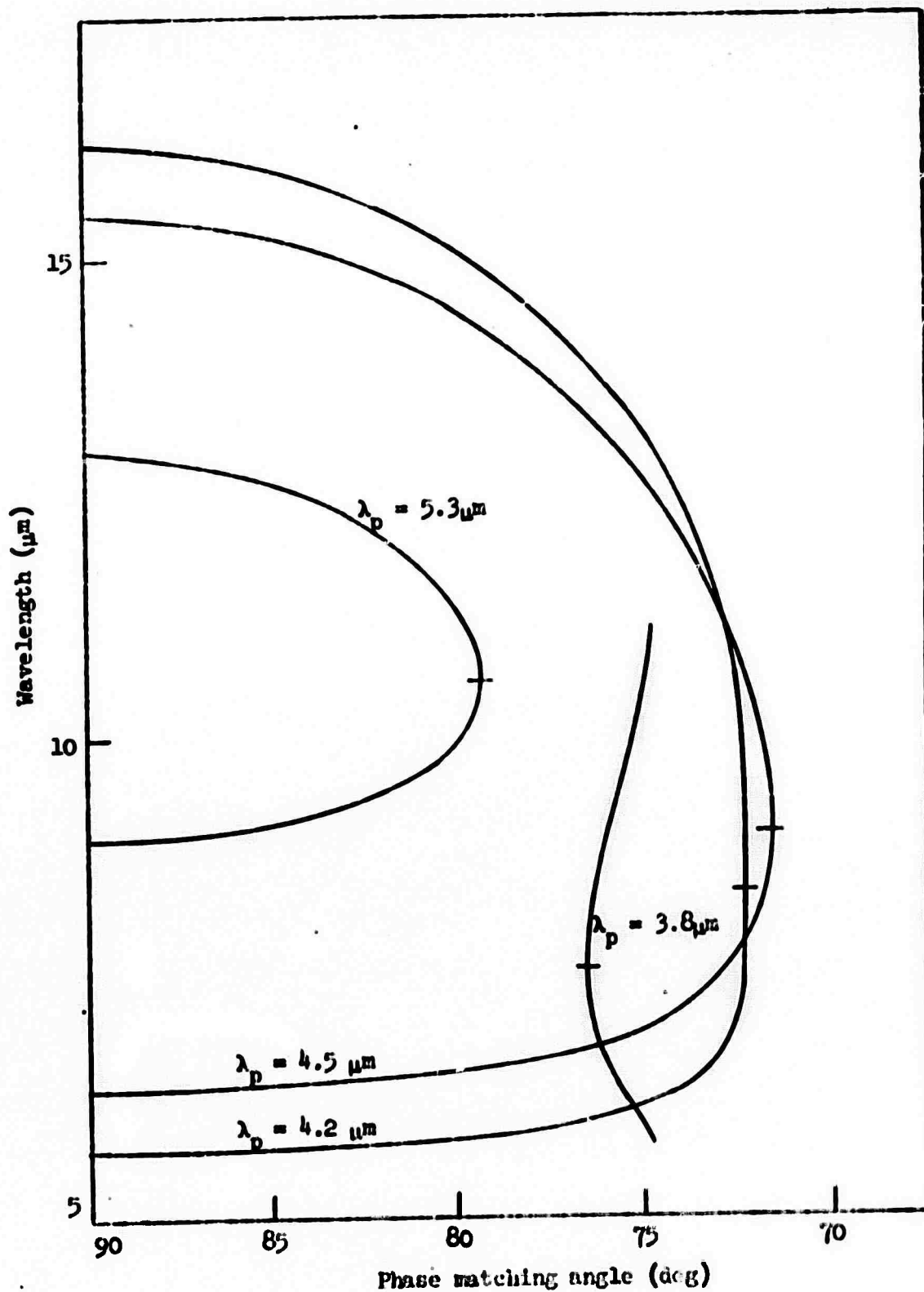
Fig. 6 - Parametric oscillator tuning waves for
various pump sources for CdGeAs₂:

V. FUTURE WORK

The primary aim of the work with $CdGeAs_2$ is to determine the experimental phasematching angle for SHG of 10.6 μ and to measure the nonlinear coefficient. If large enough single crystals become available, the sample will be used to do efficient SHG of a Q-switched CO_2 laser. For this work, a crystal need be only 2 mm long to be useful.

At the time $CdGeAs_2$ becomes available, work toward the construction of a parametric oscillator will begin. From the expected nonlinear coefficient, the power density for 30% excess gain with a 5.3 μ pump is only .67 MW/cm^2 for a 1 cm long crystal. This corresponds to 180 watts for confocal focussing. If the crystal quality can be maintained for the length of the single crystal, then a SHG Q-switched CO_2 laser should provide enough power to construct a parametric oscillator. The power density to achieve 30% parametric gain is identical to that needed to achieve 30% SHG conversion. Therefore, a 1 cm long crystal within a CO_2 laser cavity will also allow optimum SHG to 5.3 μ . These results depend upon high crystal quality and every effort will be made to obtain samples that meet the optical quality requirements.

For this reason and because we expect that it may also phasematch in the infrared, we intend to investigate the growth of $CdGeP_2$ in parallel to our present work with $CdGeAs_2$.

$CdGeP_2$ in addition to a large birefringence is transparent to 7000 Å. Thus, it allows the possibility of efficient up-conversion from the 10 μ region to 9000 Å wavelength with a Nd:YAG laser pump. This is a very important result since it may allow infrared image conversion as well as

sensitive signal detection. At the present time, proustite is the only available material that allows up-conversion. However, its small nonlinearity and low burn density limit the maximum up-conversion efficiency to only 0.001. The much greater nonlinearity of $CdGeP_2$ allows a factor of 56 improvement in up-conversion efficiency to .056 for the same power density. If $CdGeP_2$ has a higher burn density than proustite, which may be the case since proustite is particularly poor in this respect, then there is a good chance that the 5.6% up-conversion efficiency could be improved. As part of the investigation of $CdGeP_2$ and $CdGeAs_2$ both the burn power density and the up-conversion efficiency will be determined.

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